Heteroleptic N_6 coordinated ruthenium(II) complexes as building blocks for the formation of discrete Ru_2Ag_2 complexes

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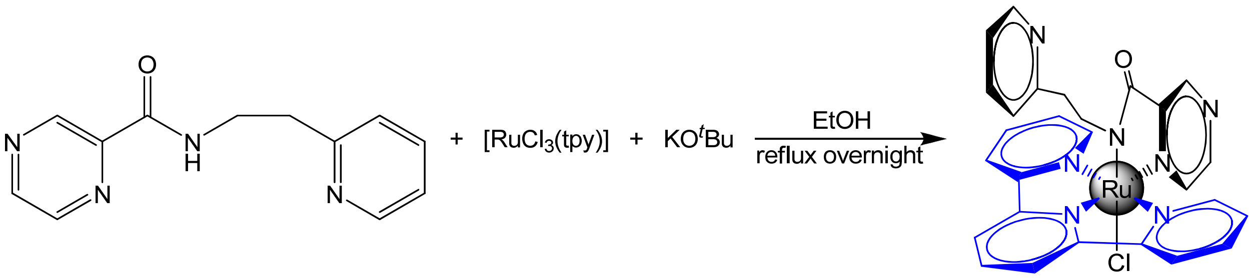
Electronic Supporting Information (ESI)

Experimental details and analytical and spectroscopic data

$[Ru^{II}Cl(L\text{-}\kappa^2)(terpy)]$ (2a)



The amide ligand H**L** (228.25 g/mol, 26 mg, 0.11 mmol, 1.0 eq) and potassium *tert*-butoxide (112.21 g/mol, 42 mg, 0.37 mmol, 3.3 eq) were degassed and stirred in 5 mL of ethanol for 30 min. The Ru precursor $[RuCl_3(terpy)]$ (440.70 g/mol, 50 mg, 0.11 mmol, 1.0 eq) was degassed, suspended in 5 mL of ethanol and treated with the solution of the deprotonated ligand (+ 5 mL of EtOH). The reaction mixture was degassed again and then refluxed overnight to afford a purple suspension. After removal of the solvent under high vacuum the residue was subjected to column chromatography on neutral alumina (~4 cm). The first sharp yellow band, eluted with CH_2Cl_2/1% of MeOH, contained just ligand. A mixture of CH_2Cl_2/2% of MeOH eluted a blue-grey and then a broad purple band which turned out to be the pure complex. A purple solid remained after removal of the solvents under high vacuum.

Conversion: 30% according to analysis of the NMR spectrum of the crude product (determined by comparison of the H-2 signals of complex **2a** and remaining free ligand. The % conversion could be improved to 56% when an amount of 18-crown-6 – equimolar to KO^tBu – was employed. However, it was difficult to get rid of the $[K(18\text{-crown-}6)]^+$ formed during the reaction).

Layering of a chloroform solution of $[RuCl(\mathbf{L}\text{-}\kappa^2)(terpy)]$ with hexane afforded dark red crystals which were suitable for X-ray analysis and proved the bidentate coordination mode of the ligand.

^{1}H-NMR (500 MHz, $CDCl_3$, rt): δ = 1.82 (m, 2H, H-11), 2.56 (m, 2H, H-10), 6.75 (br d, *J* = 7.8 Hz, 1H, H-13), 6.86 (ddd, *J* = 7.5/4.9/1.1 Hz, 1H, H-15), 7.20 (ddd, *J* = 7.3/5.7/1.3 Hz, 2H, H-b), 7.29 (dt, *J* = 7.6/1.9 Hz, 1H, H-14), 7.69 (m, 4H, H-a/H-c), 7.78 (t, *J* = 8.0 Hz, 1H, H-h), 8.06 (br d, *J* = 7.8 Hz, 2H, H-d), 8.15 (d, *J* = 8.1 Hz, 2H, H-g), 8.17 (ddd, *J* = 4.9/1.8/0.9 Hz, 1H, H-16), 8.78 (d, *J* = 3.2 Hz, 1H, H-3), 9.37 (d, *J* = 1.2 Hz, 1H, H-5), 10.14 (dd, *J* = 3.2/1.3 Hz, 1H, H-2) ppm

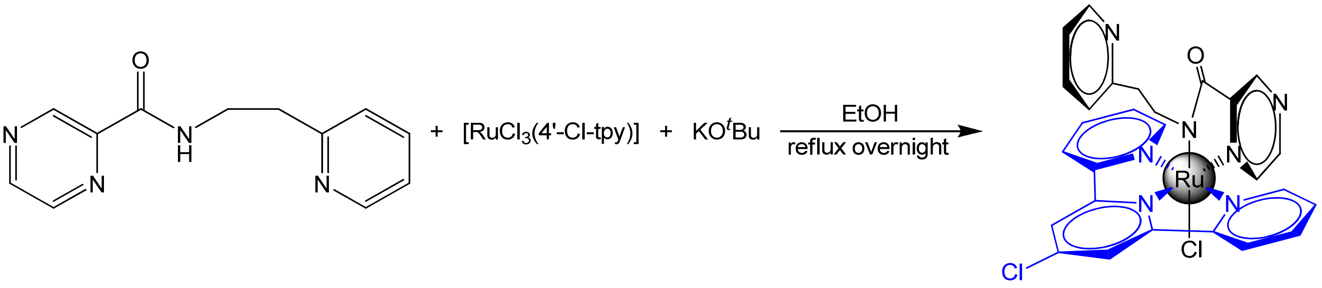
^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$, rt): δ = 37.9 (s, C-11), 47.0 (s, C-10), 120.5 (s, C-15), 120.9 (s, C-g), 122.0 (s, C-d), 122.5 (s, C-13), 126.6 (s, C-b), 130.9 (s, C-h), 135.0 (s, C-c), 135.7 (s, C-14), 145.3 (s, C-2), 145.8 (s, C-3), 146.2 (s, C-5), 148.7 (s, C-16), 151.8 (s, C-a), 152.0 (s, C-6), 157.4 (s, C-f), 158.5 (s, C-e), 160.1 (s, C-12), 169.1 (s, C-7) ppm

MS (ESI): m/z = 598.0663 (calcd. 598.0694, $[M+H]^+$, 100%), 562.1 ($[M–Cl]^+$, 11%), 281.5 ($[M+H–Cl]^{2+}$, 5%)

IR (KBr): $\tilde{\nu}$ = 3408 (br, s), 3059 (w), 2965 (w), 2921 (w), 2852 (w), 2226 (w), 1592 (vs, amide CO), 1564 (vs), 1474 (w), 1444 (s), 1380 (s), 1373 (s), 1343 (w), 1277 (m), 1245 (w), 1181 (m), 1154 (w), 1098 (w), 1051 (m), 1029 (m), 1009 (w), 881 (w), 854 (w), 768 (s), 731 (w), 724 (w), 645 (s), 618 (w), 545 (w), 522 (w), 493 (w), 468 (w) cm^{-1}

UV-vis (qualitative): λ_{max} = 542 nm, 425 nm

[Ru^{II}Cl(L-κ^2)(4'-Cl-terpy)] (2b)



The amide ligand H**L** (228.25 g/mol, 24 mg, 0.11 mmol, 1.0 eq) and potassium *tert*-butoxide (112.21 g/mol, 28 mg, 0.25 mmol, 2.4 eq) were degassed and stirred in 5 mL of ethanol for 30 min. The Ru precursor [RuCl$_3$(4'-Cl-terpy)] (475.14 g/mol, 50 mg, 0.11 mmol, 1.0 eq) was degassed, suspended in 5 mL of ethanol and treated with the solution of the deprotonated ligand (+ 5mL of EtOH). The reaction mixture was degassed again and then refluxed overnight to afford a purple suspension. After removal of the solvent under high vacuum the residue was subjected to column chromatography on neutral alumina (~5 cm). A mixture of CH_2Cl_2/2% of MeOH eluted the product as broad purple band. A solid of the same colour remained after removal of the solvents under high vacuum.

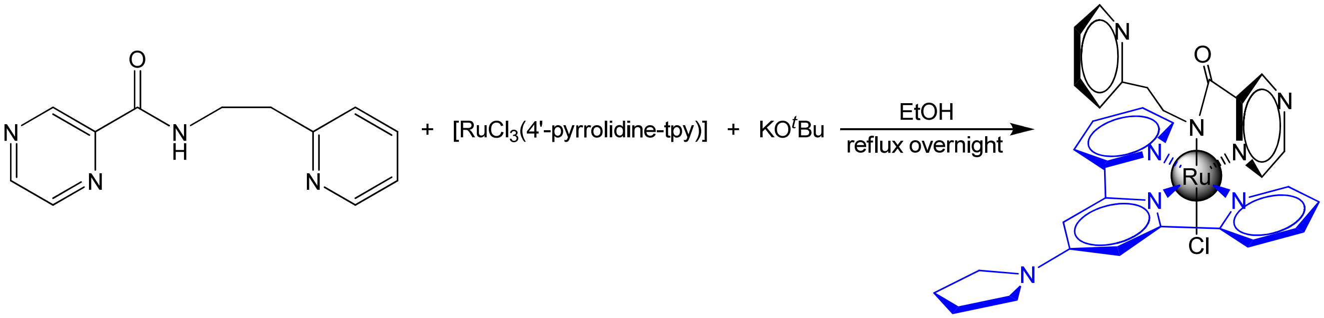
Conversion: 41% according to analysis of the NMR spectrum of the crude product (determined by comparison of the H-2 signals of complex **2b** and remaining free ligand).

^{1}H-NMR (400 MHz, $CDCl_3$, rt): δ = 1.79 (m, 2H, H-11), 2.53 (m, 2H, H-10), 6.75 (br d, *J* = 7.8 Hz, 1H, H-13), 6.90 (ddd, *J* = 7.5/4.9/1.1 Hz, 1H, H-15), 7.23 (ddd, *J* = 7.3/5.7/1.3 Hz, 2H, H-b), 7.31 (dt, *J* = 7.6/1.9 Hz, 1H, H-14), 7.71 (m, 4H, H-a/H-c), 8.04 (m, 2H, H-d), 8.14 (s, 2H, H-g), 8.23 (ddd, *J* = 4.9/1.8/0.9 Hz, 1H, H-16), 8.80 (d, *J* = 3.2 Hz, 1H, H-3), 9.37 (d, *J* = 1.2 Hz, 1H, H-5), 10.11 (dd, *J* = 3.2/1.3 Hz, 1H, H-2) ppm

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$, rt): δ = 37.9 (s, C-11), 47.0 (s, C-10), 120.6 (s, C-15), 121.3 (s, C-g), 122.5 (s, C-d), 122.5 (s, C-13), 127.1 (s, C-b), 135.1 (s, C-c), 135.8 (s, C-14), 138.4 (s, C-h), 145.3 (s, C-2), 145.9 (s, C-3), 146.3 (s, C-5), 148.9 (s, C-16), 151.8 (s, C-6), 151.9 (s, C-a), 157.6 (s, C-e), 158.2 (s, C-f), 159.8 (s, C-12), 169.0 (s, C-7) ppm

MS (ESI): m/z = 632.0 ([M+H]$^+$, 100%)

[Ru^{II}Cl(L-κ^2)(4'-pyrrolidine-terpy)] (2c)



The amide ligand H**L** (228.25 g/mol, 22 mg, 0.10 mmol, 1.0 eq) and potassium *tert*-butoxide (112.21 g/mol, 26 mg, 0.24 mmol, 2.4 eq) were degassed and stirred in 5 mL of ethanol for 30 min. The Ru precursor [RuCl$_3$(4'-pyrrolidine-terpy)] (509.80 g/mol, 50 mg, 0.10 mmol, 1.0 eq) was degassed, suspended in 5 mL of ethanol and treated with the solution of the deprotonated ligand (+ 5mL of EtOH). The reaction mixture was degassed again and then refluxed overnight to afford a purple suspension. After removal of the solvent under high vacuum the residue was subjected to column chromatography on neutral alumina (~5 cm). A mixture of CH_2Cl_2/2% of MeOH eluted the product as broad purple band. A blue-grey solid remained after removal of the solvents under high vacuum.

Conversion: 27% according to analysis of the NMR spectrum of the crude product (determined by comparison of the H-2 signals of complex **2c** and remaining free ligand).

^{1}H-NMR (400 MHz, $CDCl_3$, rt): δ = 1.97 (m, 2H, H-11), 2.17 (m, 4H, H-pyrr), 2.75 (m, 2H, H-10), 3.61 (m, 4H, H-pyrr), 6.85 (ddd, *J* = 7.8/4.9/1.2 Hz, 1H, H-15), 6.89 (br d, *J* = 7.8 Hz, 1H, H-13), 7.07 (ddd, *J* = 7.5/5.5/1.3 Hz, 2H, H-b), 7.30 (dt, *J* = 7.6/1.8 Hz, 1H, H-14), 7.31 (s, 2H, H-g), 7.60 (dt, *J* = 7.8/1.5 Hz, 2H, H-c), 7.67 (br d, *J* = 5.5 Hz, 2H, H-a), 7.95 (br d, *J* = 7.8 Hz, 2H, H-d), 8.15 (ddd, *J* = 4.9/1.8/0.9 Hz, 1H, H-16), 8.62 (d, *J* = 3.3 Hz, 1H, H-3), 9.26 (d, *J* = 1.3 Hz, 1H, H-5), 10.09 (dd, *J* = 3.3/1.3 Hz, 1H, H-2) ppm

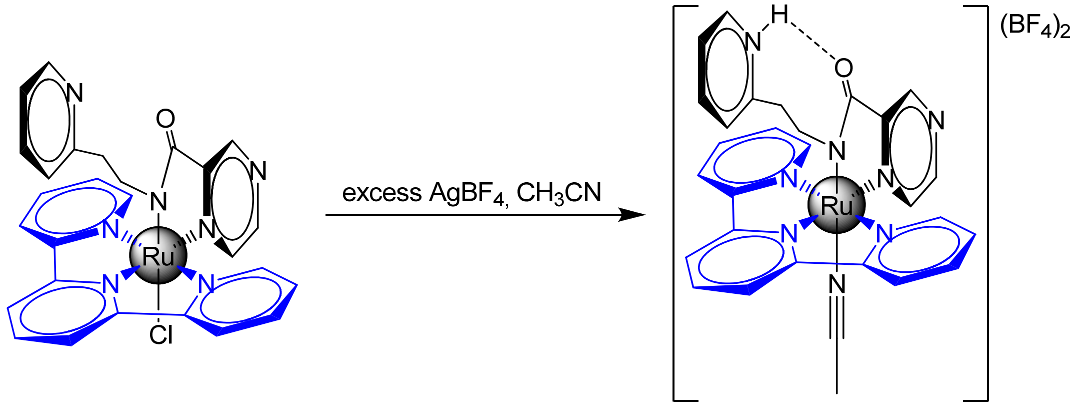
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, rt): δ = 25.5 (s, C-pyrr), 37.8 (s, C-11), 46.8 (s, C-10), 48.0 (s, C-pyrr), 104.9 (s, C-g), 120.4 (s, C-15), 121.7 (s, C-d), 122.7 (s, C-13), 126.0 (s, C-b), 134.3 (s, C-c), 135.7 (s, C-14), 145.2 (s, C-3), 145.9 (s, C-5), 146.3 (s, C-2), 148.5 (s, C-16), 150.8 (s, C-h), 152.1 (s, C-a), 153.4 (s, C-6), 155.8 (s, C-e), 159.3 (s, C-f), 160.6 (s, C-12), 169.8 (s, C-7) ppm

MS (ESI): m/z = 689.1012 (calcd. 689.1231, $[M+Na]^+$, 53%), 667.1200 (calcd. 667.1269, $[M+H]^+$, 81%), 631.1444 (calcd. 631.1502, $[M–Cl]^+$, 100%), 535.0859 (calcd. 535.0880, $[Ru_2(C_{12}H_{11}N_4O)(C_{19}H_{18}N_4)_2Cl]^{2+}$, 25%)

IR (KBr): $\tilde{\nu}$ = 3408 (br, s), 3054 (w), 2921 (m), 2847 (m), 2211 (w), 1619 (vs), 1589 (vs), 1557 (s), 1498 (s), 1481 (s), 1439 (s), 1370 (m), 1353 (m), 1289(w), 1274 (m), 1247 (w), 1230 (w), 1181 (m), 1144 (w), 1110 (w), 1090 (w), 1056 (m), 1036 (m), 1009 (w), 918 (w), 852 (m), 783 (s), 753 (m), 721 (m), 643 (s), 616 (w), 520 (w), 451 (w) cm^{-1}

UV-vis (qualitative): λ_{max} = 543 nm, 468 nm, 427 nm, 283 nm, 235 nm (s)

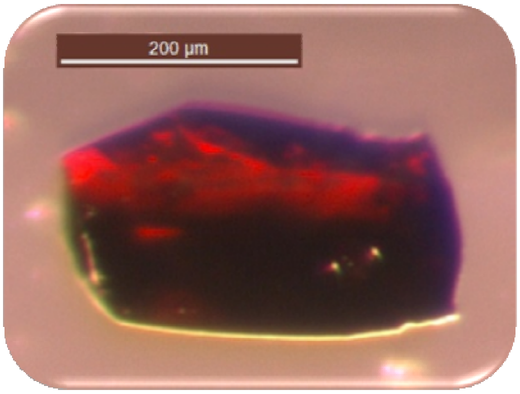
$[Ru^{II}(H+L\text{-}\kappa^2)(CH_3CN)(terpy)](BF_4)_2$ (3a)

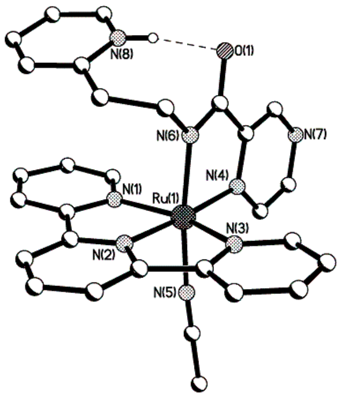


Complex [RuCl(**L**-κ^2)(terpy)], prepared and purified as described above, was dissolved in 5 mL of acetonitrile and treated with an excess of $AgBF_4$. The purple reaction mixture was refluxed overnight. The white precipitate was then filtered off through celite and the solvent of the red solution removed under high vacuum. To obtain the pure mononuclear complex **3a** (rather than the tetranuclear Ru_2Ag_2 compound **4**, vide infra) the excess $AgBF_4$ has to be removed by washing with THF and CH_2Cl_2 before crystallisation.

Conversion: quantitative according to analysis of the NMR spectrum (just one set of signals).

Crystals of [Ru(H+**L**-κ^2)(CH_3CN)(terpy)]$(BF_4)_2$ **3a** were obtained by over-layering an MeCN solution by Et_2O.





^{1}H-NMR (500 MHz, CD_3CN, rt): δ = 1.92 (m, 2H, H-11), 2.01 (s, 3H, CH_3CN), 2.53 (m, 2H, H-10), 6.78 (d, *J* = 7.9 Hz, 1H, H-13), 7.26 (dd, *J* = 6.5/5.6 Hz, 1H, H-15), 7.40 (ddd, *J* = 7.5/5.5/1.3 Hz, 2H, H-b), 7.70 (dt, *J* = 7.7/1.5 Hz, 1H, H-14), 7.78 (ddd, *J* = 5.5/1.4/0.6 Hz, 2H, H-a), 8.00 (dt, *J* = 7.8/1.5 Hz, 2H, H-c), 8.22 (t, *J* = 8.1 Hz, 1H, H-h), 8.37 (br d, *J* = 4.8 Hz, 1H, H-16), 8.41 (br d, *J* = 8.0 Hz, 2H, H-d), 8.52 (d, *J* = 8.1 Hz, 2H, H-g), 8.91 (d, *J* = 3.2 Hz, 1H, H-3), 9.34 (d, *J* = 1.1 Hz, 1H, H-5), 9.47 (dd, *J* = 3.2/1.2 Hz, 1H, H-2) ppm

^{13}C{^{1}H}-NMR (125 MHz, CD_3CN, rt): δ = 4.3 (s, $\underline{C}H_3CN$), 40.1 (s, C-11), 46.7 (s, C-10), 123.5 (s, $CH_3\underline{C}N$), 123.7 (s, C-15), 123.9 (s, C-g), 124.8 (s, C-d), 125.3 (s, C-13), 128.9 (s, C-b), 136.8 (s, C-h), 139.0 (s, C-c), 140.6 (s, C-14), 147.2 (s, C-2), 147.3 (s, C-3), 148.2 (s, C-5), 150.1 (br s, C-16), 152.4 (s, C-6), 153.9 (s, C-a), 158.2 (s, C-f), 159.2 (s, C-e), 159.2 (s, C-12), 170.2 (s, C-7) ppm

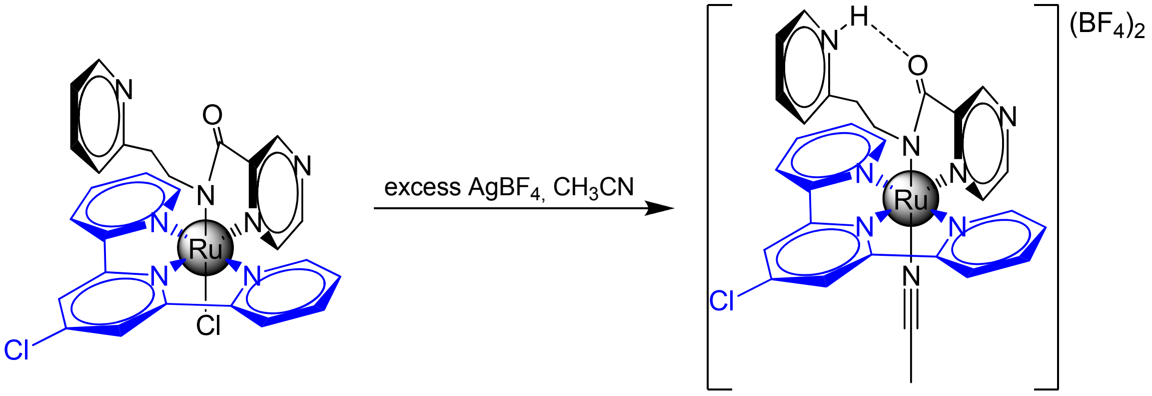
MS (ESI): m/z = 603.1 (M^+, 1%), 562.0934 (calcd. 562.0931, $[M–CH_3CN]^+$, 2%), 281.5 ($[M+H–CH_3CN]^{2+}$, 100%)

IR (KBr): $\tilde{\nu}$ = 3438 (br, vs), 3059 (w), 2921 (w), 2852 (w), 2714 (w), 2684 (w), 2359 (w), 1611 (vs, amide CO), 1466 (w), 1447 (m), 1415 (w), 1388 (m), 1373 (w), 1346 (w), 1304 (w), 1287 (w), 1245 (w), 1122/1083/1034 (vs, BF_4^-), 854 (w), 768 (m), 734 (w), 645 (m), 532 (m), 520 (m) cm^{-1}

UV-vis (ε [$M^{-1}\cdot cm^{-1}$]): λ_{max} = 480 nm (9610), 421 nm (6710), 388 nm (6030), 313 nm (25770), 270 nm (26700), 232 nm (33430), 213 nm (38200)

Elemental analysis for [Ru(H+**L**-*κ*^{2})(CH_3CN)(terpy)]$(BF_4)_2$ = $C_{29}H_{26}B_2F_8N_8ORu$ (777.25 g/mol): calcd. C 44.81, H 3.37, N 14.42; found: C 44.93, H 3.20, N 14.19

[Ru^{II}(H+L-*κ*^{2})(CH_3CN)(4'-Cl-terpy)]$(BF_4)_2$ (3b)



Complex [RuCl(**L**-*κ*^{2})(4'-Cl-terpy)], prepared and purified as described above, was dissolved in 5 mL of acetonitrile and treated with an excess of $AgBF_4$. The purple reaction mixture was refluxed overnight. The white precipitate was then filtered off through celite and the solvent of the red solution removed under high vacuum. The excess $AgBF_4$ has to be removed by washing with THF and CH_2Cl_2 before crystallisation.

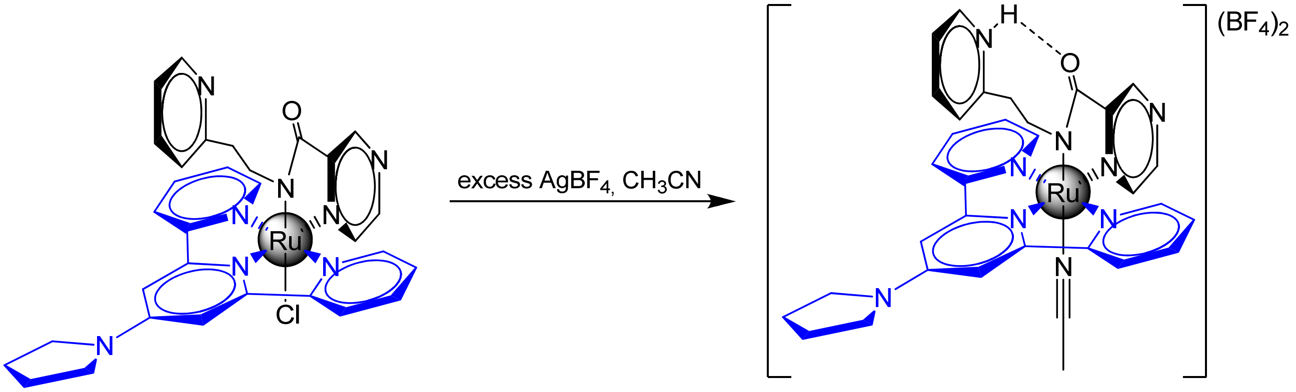
Conversion: quantitative according to analysis of the NMR spectrum (just one set of signals)

^{1}H-NMR (400 MHz, CD_3CN, rt): δ = 1.86 (m, 2H, H-11), 2.00 (s, 3H, CH_3CN), 2.51 (m, 2H, H-10), 6.76 (d, *J* = 7.7 Hz, 1H, H-13), 7.20 (vt, *J* = 6.5 Hz, 1H, H-15), 7.44 (ddd, *J* = 7.6/5.5/1.3 Hz, 2H, H-b), 7.62 (vt, *J* = 7.5 Hz, 1H, H-14), 7.79 (ddd, *J* = 5.5/1.5/0.7 Hz, 2H, H-a), 8.03 (dt, *J* = 7.9/1.5 Hz, 2H, H-c), 8.29 (br d, *J* = 5.0 Hz, 1H, H-16), 8.40 (br d, *J* = 7.6 Hz, 2H, H-d), 8.61 (s, 2H, H-g), 8.91 (d, *J* = 3.2 Hz, 1H, H-3), 9.29 (d, *J* = 1.2 Hz, 1H, H-5), 9.43 (dd, *J* = 3.2/1.2 Hz, 1H, H-2) ppm

^{13}C{^{1}H}-NMR (125 MHz, CD_3CN, rt): δ = 40.1 (s, C-11), 40.9 (s, C-10), 124.3 (s, C-g), 125.5 (s, C-d), 129.4 (s, C-b), 139.1 (s, H-c), 144.0 (s, C-h), 147.1 (s, C-5), 148.2 (s, C-2), 148.2 (s, C-3), 151.9 (s, C-6), 154.1 (s, C-a), 158.1 (s, C-e), 158.9 (s, C-f), 170.1 (s, C-7) ppm (the signals of the dangling pyridine ring and the coordinated acetonitrile molecule could not be determined unambiguously).

MS (ESI): m/z = 637.1 (M^+, 3%), 596.1 ($[M–CH_3CN]^+$, 4%), 298.5323 (calcd. 298.5305, $[M+H–CH_3CN]^{2+}$, 100%)

[Ru^{II}(H+L-*κ*^{2})(CH$_3$CN)(4'-pyrrolidine-terpy)](BF$_4$)$_2$ (3c)



Complex [RuCl(**L**-*κ*^{2})(4'-pyrrolidine-terpy)], prepared and purified as described above, was dissolved in 5 mL of acetonitrile and treated with an excess of AgBF$_4$. The purple reaction mixture was refluxed for six hours. The white precipitate was then filtered off through celite and the solvent of the red solution removed under high vacuum. The excess AgBF$_4$ has to be removed by washing with THF and CH$_2$Cl$_2$ before crystallisation.

Conversion: quantitative according to analysis of the NMR spectrum (just one set of signals).

^{1}H-NMR (500 MHz, CD$_3$CN, rt): δ = 2.20 (m, 4H, H-pyrr), 2.21 (m, 2H, H-11), 2.86 (m, 2H, H-10), 3.73 (m, 4H, H-pyrr), 7.24 (br d, *J* = 7.8 Hz, 1H, H-13), 7.26 (ddd, *J* = 7.7/5.5/1.2 Hz, 2H, H-b), 7.60 (m, 1H, H-15), 7.64 (s, 2H, H-g), 7.69 (br d, *J* = 5.5 Hz, 2H, H-a), 7.95 (dt, *J* = 7.9/1.6 Hz, 2H, H-c), 8.08 (dt, *J* = 7.9/1.6 Hz, 1H, H-14), 8.39 (br d, *J* = 8.1 Hz, 2H, H-d), 8.45 (br d, *J* = 5.7 Hz, 1H, H-16), 8.86 (d, *J* = 3.1 Hz, 1H, H-3), 9.23 (d, *J* = 1.1 Hz, 1H, H-5), 9.44 (dd, *J* = 3.1/1.1 Hz, 1H, H-2) ppm

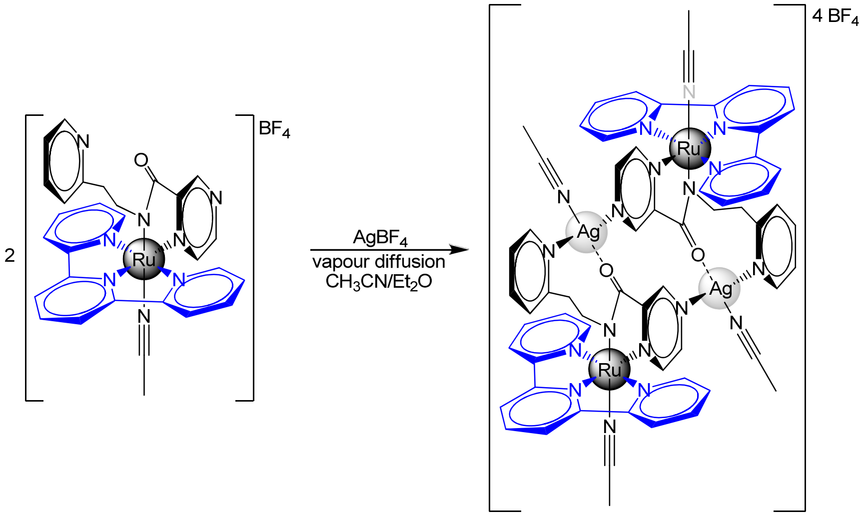
^{13}C{^{1}H}-NMR (125 MHz, CD$_3$CN, rt): δ = 4.33 (s, $\underline{C}H_3CN$), 26.1 (s, C-pyrr), 37.0 (s, C-11), 44.1 (s, C-10), 49.3 (C-pyrr), 107.4 (s, C-g), 124.1 (s, C-d), 124.3 (br s, $CH_3\underline{C}N$), 125.2 (s, C-15), 127.4 (s, C-13), 128.1 (s, C-b), 138.6 (s, C-c), 142.4 (s, C-16), 145.3 (s, C-14), 147.0 (s, C-5), 147.6 (s, C-2), 148.3 (s, C-3), 152.0 (s, C-6), 154.2 (s, C-a), 155.8 (s, C-f), 156.3 (s, C-12), 159.9 (s, C-e), 171.1 (s, C-7) ppm

MS (ESI): m/z = 631.1511 (calcd. 631.1502, [M–CH$_3$CN]$^+$, 100%)

IR (KBr): $\tilde{\nu}$ = 3438 (br, vs), 3059 (w), 2921 (w), 2852 (w), 2714 (w), 2684 (w), 2359 (w), 1611 (vs, amide CO), 1466 (w), 1447 (m), 1415 (w), 1388 (m), 1373 (w), 1346 (w), 1304 (w), 1287 (w), 1245 (w), 1122/1083/1034 (vs, BF$_4^-$), 854 (w), 768 (m), 734 (w), 645 (m), 532 (m), 520 (m) cm^{-1}

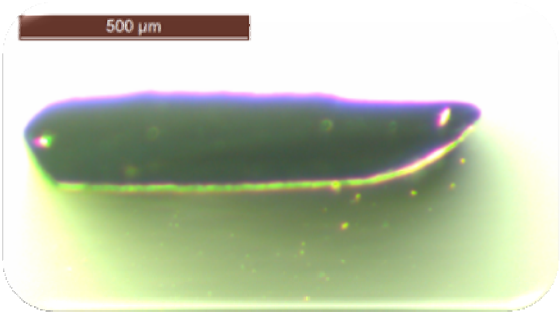
UV-vis (qualitative): λ$_{max}$ = 473 nm, 326 nm (s), 293 nm, 272 nm, 231 nm, 201 nm

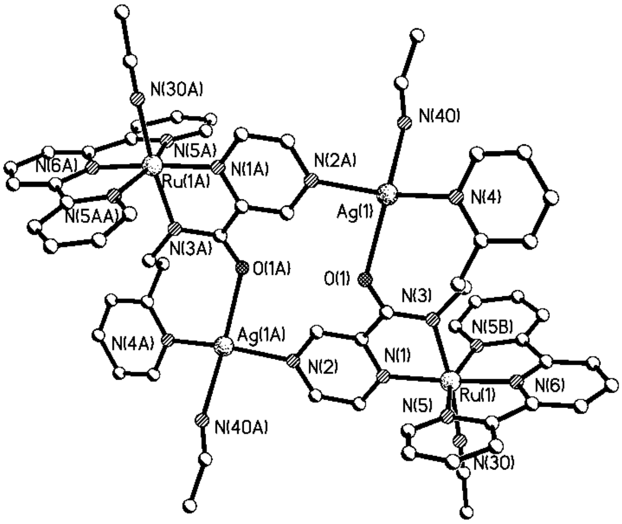
[{Ru^{II}(L-*κ*^{2})(CH$_3$CN)(terpy)}$_2${Ag(CH$_3$CN)}$_2$](BF$_4$)$_4$ (4)



Layering of an acetonitrile solution of [Ru(H+**L**-κ^2)(CH_3CN)(terpy)](BF_4)$_2$ **3a** and an excess of $AgBF_4$ with diethyl ether afforded turquoise crystals which were determined to be the tetranuclear complex [{Ru(**L**-κ^2)(CH_3CN)(terpy)}$_2${Ag(CH_3CN)}$_2$](BF_4)$_4$ ·Et_2O, **4**·Et_2O.

Yield: 40%



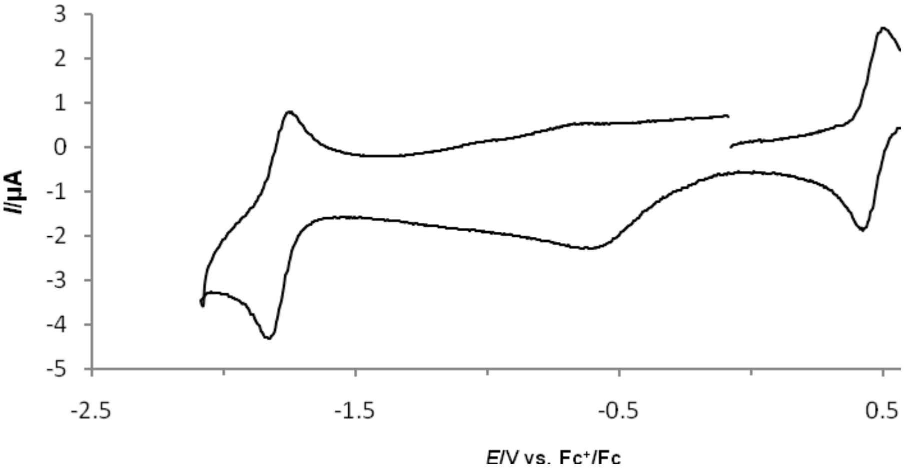


IR (KBr): $\tilde{\nu}$ = 3438 (vs), 1621 (vs, amide CO), 1596 (vs), 1508 (s), 1444 (m), 1370 (w), 1351 (w) 1083 (vs, BF_4^-), 783 (s) cm^{-1}

UV-vis (qualitative): λ_{max} = 481 nm, 420 nm, 387 nm, 313 nm, 269 nm, 233 nm, 211 nm. The absorption coefficients could not be calculated as the concentration of the solution was not determined. Nevertheless these λ_{max} values reflect the values found for **3a** and thus indicates that **4** dissociates upon dissolving.

Elemental analysis for [{Ru(**L**-κ^2)(CH_3CN)(terpy)}$_2${Ag(CH_3CN)}$_2$](BF_4)$_4$·Et_2O **4**·Et_2O after drying was consistent with the hydrate [$Ag_2Ru_2(CH_3CN)_2(C_{15}N_3H_{11})_2(C_{12}H_{11}N_4O)_2$]($BF_4$)$_4$·3.5$H_2O$ ($C_{58}H_{57}Ag_2B_4F_{16}N_{16}O_{5.5}Ru_2$;1831.27 g/mol): calcd. C 38.04, H 3.14, N 12.24; found: C 38.21, H 3.22, N 11.99.

Electrochemistry of **3a**:



Full cyclic voltammogram of **3a** in MeCN at 200 mV/s (0.1 M Bu_4NPF_6).